Graded Orthogonality for Fermionic States

Patrick CASSAM-CHENAÏ

Laboratoire J. A. Dieudonné, UMR-6621 du CNRS
et de l' Université de Nice - Sophia-Antipolis

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Notation-1

- $\mathcal{H}$: Hilbert space of one-electron functions, spanned by a set of spin-orbitals $(\psi_i)_i$

- $\wedge^n\mathcal{H}$: Hilbert space of n-electron antisymmetric functions, spanned by the Slater determinantal functions $(\psi_{i_1} \wedge \psi_{i_2} \wedge \cdots \wedge \psi_{i_n})_{(i_1<i_2<\cdots<i_n)}$

- $\wedge\mathcal{H}$: Fermionic Fock space

$$\wedge\mathcal{H} := \bigoplus_{n\geq 0} \wedge^n\mathcal{H}$$

- $\wedge^{n_1}\mathcal{H} \otimes \cdots \otimes \wedge^{n_k}\mathcal{H}$: Hilbert space of partially antisymmetric functions for k distinguishable groups of electrons of respectively $n_1, \dots, n_k$ electrons

Notation-2

- For any n-particle wave function, $\Phi := \sum_{I:=(i_1<\ldots<i_n)} c_I \, \psi_{i_1} \wedge \cdots \wedge \psi_{i_n}$,

- and any ordered sequence of length p, $K := (k_1 < \ldots < k_p) \in \mathcal{P}_{n,p}$, with $p \in \{0, \ldots, n\}$, $1 \leq k_j \leq n$,

- we set,

$$\cdots(\Phi)_K\cdots(\Phi)_{\bar{K}}\cdots := \rho_{K,\bar{K}} \sum_{I:=(i_1<\cdots<i_n)} c_I \cdots(\psi_{i_{k_1}} \wedge \cdots \wedge \psi_{i_{k_p}})\cdots(\psi_{i_{\bar{k}_1}} \wedge \cdots \wedge \psi_{i_{\bar{k}_{n-p}}})\cdots$$

- where $\bar{K} := (\bar{k}_1 < \ldots < \bar{k}_{n-p})$, complement of K in $(1 < 2 < \cdots < n)$, $\rho_{K,\bar{K}}$ is the sign of the permutation reordering the concatenated sequence $K//\bar{K}$ in increasing order; if the length, $|K|$, of K is 0 then, by convention, $(\Phi)_K := (\Phi)_\emptyset = 1$, and $\rho_{\emptyset,(1<\cdots<n)} = 1$; note that, $(\Phi)_{(1<\cdots<n)} = \Phi$.

Grassmann's exterior product:

$$\begin{aligned}\mathcal{X} : \wedge\mathcal{H} \otimes \wedge\mathcal{H} &\longmapsto \wedge\mathcal{H} \\ \Phi \otimes \Psi &\longrightarrow \mathcal{X}(\Phi \otimes \Psi) = \Phi \wedge \Psi\end{aligned}$$

The fermionic symmetry is built-in in this exterior algebra because of the following antisymmetry relation between exterior products of 1-particle functions:

$$\mathcal{X}(\phi \otimes \psi) = \phi \wedge \psi = -\psi \wedge \phi = -\mathcal{X}(\psi \otimes \phi)$$

which entirely determines the behavior of an n-fermion wave function under the symmetric group $\mathcal{S}_n$. That is to say, for an n-fermion single configuration:

$$\psi_1 \wedge \cdots \wedge \psi_n = (-1)^{|\sigma|} \psi_{\sigma(1)} \wedge \cdots \wedge \psi_{\sigma(n)}$$

Conjugate interior products:

$\forall \Theta \in \wedge^{n-p}\mathcal{H},\ \forall \Psi \in \wedge^{p}\mathcal{H},\ \forall \Phi \in \wedge^{n}\mathcal{H},$

- "left-interior product" $\langle \Theta | \Psi \hookleftarrow \Phi \rangle = \langle \Psi \wedge \Theta | \Phi \rangle$
- "right-interior product" $\langle \Theta | \Phi \hookrightarrow \Psi \rangle = \langle \Theta \wedge \Psi | \Phi \rangle$
- "anti-commutativity" $\Psi \hookleftarrow \Phi = (-1)^{p(n-p)}\ \Phi \hookrightarrow \Psi$
- explicit formula

$$\Psi \hookleftarrow \Phi = \sum_{K \in \mathcal{P}_{n,p}} \langle \Psi | \Phi_K \rangle \cdot \Phi_{\bar{K}}$$

- or for mono-configuration functions (Slater determinants)

$$(\psi_1 \wedge \cdots \wedge \psi_p) \hookleftarrow (\phi_1 \wedge \cdots \wedge \phi_n) = \sum_{K \in \mathcal{P}_{n,p}} \rho_{K,\bar{K}}\, det(\langle \psi_i | \phi_{k_j} \rangle)_{i,j \leq p}\, \phi_{\bar{k}_1} \wedge \cdots \wedge \phi_{\bar{k}_{n-p}}$$

1-internal space of a wave function

Definition:

$$\mathcal{I}^1[\Psi] = \{\omega \in \mathcal{H}, \exists \Phi \in \wedge^{n-1}\mathcal{H}, \Phi \hookleftarrow \Psi = \omega\}$$

Example:

$$\begin{aligned}
\Psi_e \quad = \quad & \frac{1}{4}\{\phi_1^\alpha \wedge \phi_3^\alpha \wedge \phi_5^\alpha \wedge \phi_1^\beta \wedge \phi_3^\beta + \phi_1^\alpha \wedge \phi_3^\alpha \wedge \phi_6^\alpha \wedge \phi_1^\beta \wedge \phi_4^\beta + \\
& \phi_1^\alpha \wedge \phi_4^\alpha \wedge \phi_6^\alpha \wedge \phi_1^\beta \wedge \phi_3^\beta + \phi_1^\alpha \wedge \phi_4^\alpha \wedge \phi_5^\alpha \wedge \phi_1^\beta \wedge \phi_4^\beta + \\
& \phi_1^\alpha \wedge \phi_3^\alpha \wedge \phi_5^\alpha \wedge \phi_2^\beta \wedge \phi_3^\beta + \phi_1^\alpha \wedge \phi_3^\alpha \wedge \phi_6^\alpha \wedge \phi_2^\beta \wedge \phi_4^\beta + \\
& \phi_1^\alpha \wedge \phi_4^\alpha \wedge \phi_6^\alpha \wedge \phi_2^\beta \wedge \phi_3^\beta + \phi_1^\alpha \wedge \phi_4^\alpha \wedge \phi_5^\alpha \wedge \phi_2^\beta \wedge \phi_4^\beta + \\
& \phi_2^\alpha \wedge \phi_3^\alpha \wedge \phi_5^\alpha \wedge \phi_1^\beta \wedge \phi_3^\beta + \phi_2^\alpha \wedge \phi_3^\alpha \wedge \phi_6^\alpha \wedge \phi_1^\beta \wedge \phi_4^\beta + \\
& \phi_2^\alpha \wedge \phi_4^\alpha \wedge \phi_6^\alpha \wedge \phi_1^\beta \wedge \phi_3^\beta + \phi_2^\alpha \wedge \phi_4^\alpha \wedge \phi_5^\alpha \wedge \phi_1^\beta \wedge \phi_4^\beta + \\
& \phi_2^\alpha \wedge \phi_3^\alpha \wedge \phi_5^\alpha \wedge \phi_2^\beta \wedge \phi_3^\beta + \phi_2^\alpha \wedge \phi_3^\alpha \wedge \phi_6^\alpha \wedge \phi_2^\beta \wedge \phi_4^\beta + \\
& \phi_2^\alpha \wedge \phi_4^\alpha \wedge \phi_6^\alpha \wedge \phi_2^\beta \wedge \phi_3^\beta + \phi_2^\alpha \wedge \phi_4^\alpha \wedge \phi_5^\alpha \wedge \phi_2^\beta \wedge \phi_4^\beta\}
\end{aligned}$$

$$\mathcal{I}^1[\Psi_e] = \mathbb{C}(\psi_1^\alpha := \frac{1}{\sqrt{2}}(\phi_1^\alpha + \phi_2^\alpha), \psi_1^\beta := \frac{1}{\sqrt{2}}(\phi_1^\beta + \phi_2^\beta), \phi_3^\alpha, \phi_3^\beta, \phi_4^\alpha, \phi_4^\beta, \phi_5^\alpha, \phi_6^\alpha)$$

Other characterizations

- Smallest one-electron Hilbert-subspace allowing one to express Ψ:

$$\forall V \subseteq \mathcal{H}, \Psi \in \wedge^n V, \mathcal{I}^1[\Psi] \subseteq V$$

Application: compact expressions

$$\Psi_e = \frac{1}{2}\psi_1^\alpha \wedge \psi_1^\beta \wedge (\phi_3^\alpha \wedge \phi_5^\alpha \wedge \phi_3^\beta + \phi_3^\alpha \wedge \phi_6^\alpha \wedge \phi_4^\beta + \phi_4^\alpha \wedge \phi_6^\alpha \wedge \phi_3^\beta + \phi_4^\alpha \wedge \phi_5^\alpha \wedge \phi_4^\beta).$$

- One-electron Hilbert-subspace spanned by the occupied natural spin-orbitals of Ψ:

Application: case of open-shell wave function, eigenfunction of S^2, but where the natural spin $\frac{1}{2}$ orbitals have are distinct spatial parts from those of the natural spin $-\frac{1}{2}$ orbitals

$\rightsquigarrow$ There exists a basis set of internal spin-orbitals such that for each spin $\frac{1}{2}$ orbital there is a spin $-\frac{1}{2}$ orbital with same spatial part.

The Complete Active Space Self-Consistent Field Method (CASSCF)

- A UCASSCF calculation with m active orbitals (and no inactive occupied) consists in finding the stationary points of the energy functionnal $E(\Psi) = \frac{\langle\Psi|H\Psi\rangle}{\langle\Psi|\Psi\rangle}$ with the constraint that $dim\mathcal{I}^1[\Psi] \leq m$ i.e. within $\{\Psi \in \wedge^n\mathcal{H} | \forall\Phi_0,\ldots,\Phi_{m-n} \in \wedge^{n-1}\mathcal{H}, (\Phi_0 \hookleftarrow \Psi) \wedge \cdots \wedge (\Phi_{m-n} \hookleftarrow \Psi) \wedge \Psi = 0\}$.

Example: Finite basis set of M spin-orbitals

$$\forall H_0,\ldots,H_{m-n} \in \mathcal{P}_{M,n-1},\ \forall G \in \mathcal{P}_{M,m+1}$$

$$\sum_{\substack{(k_0<\cdots<k_{m-n})\subseteq G,\\ \{k_i\}\not\subseteq H_i}} \rho_{(k_0),H_0}\cdots\rho_{(k_{m-n}),H_{m-n}}\ \rho_{(k_0<\cdots<k_{m-n}),G\setminus(k_0<\cdots<k_{m-n})}$$

$$c_{(k_0)\cup H_0}\cdots c_{(k_{m-n})\cup H_{m-n}}\ c_{G\setminus(k_0<\cdots<k_{m-n})} = 0$$

- The case $m = n$ with no spin constraint is the UHF method first developed by Prof. Berthier (and not Pople as found in textbooks).

Variational spaces of traditional methods

$$\Phi = \phi_1^\alpha \Lambda \phi_1^\beta + \beta \phi_1^\alpha \Lambda \phi_2^\beta + \gamma \phi_2^\alpha \Lambda \phi_1^\beta + \delta \phi_2^\alpha \Lambda \phi_2^\beta$$

The three, real, parameters β, γ, δ are considered as independent and varying on $]-\infty, +\infty[$ and an axis is associated with each parameter. In the 3-dimensional space obtained, UHF wave functions satisfy :

$$\beta\gamma = \delta\,,$$

which is clearly the equation of a set of hyperbolae. Singlet wave functions satisfy : $\beta = \gamma\,.$

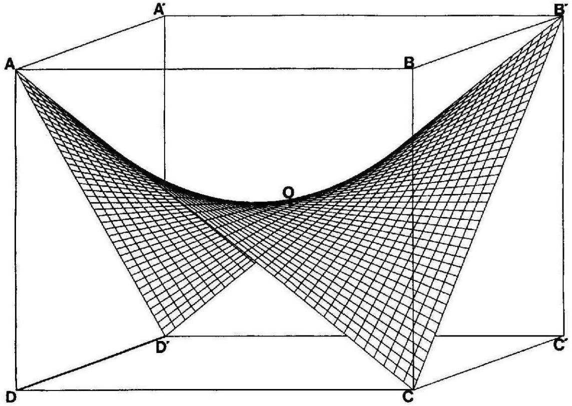

Fig. 1. 2 electrons, 2 orbitals, $S_z = 0$. Each point in the cube corresponds to a multi-configuration, the centre of the cube O being the configuration $\phi_1^\alpha \Lambda \phi_1^\beta$. The volume of the cube is the full unrestricted CI space, the hyperbolic surface $(AOB'CD')$ is the UHF space. The plane $(ADB'C')$ corresponds to the eigenfunctions of $\mathbf{S}^2$ with $S = 0$ (singlet plane). The intersection between the UHF surface and the singlet plane gives the RHF curve (AOB').

Strong orthogonality

Let Ψ_1 be the wave functions of an n_1 electron group and Ψ_2 that of an n_2 electron group. Ψ_1 and Ψ_2 are said strongly orthogonal if and only if: $\forall \tau_2, \ldots, \tau_{n_1}, \tau'_2, \ldots, \tau'_{n_2}$

$$\int d\tau_1 \Psi_1(\tau_1, \tau_2, \ldots, \tau_{n_1}) \Psi_2(\tau_1, \tau'_2, \ldots, \tau'_{n_2}) = \langle \delta_{\tau_2} \wedge \ldots \wedge \delta_{\tau_{n_1}} \hookleftarrow \Psi_1 | \delta_{\tau'_2} \wedge \ldots \wedge \delta_{\tau'_{n_2}} \hookleftarrow \Psi_2 \rangle = 0.$$

Or by changing to a basis set representation $\{\phi_i\}_i$,

$$\langle \phi_{i_2} \wedge \ldots \wedge \phi_{i_{n_1}} \hookleftarrow \Psi_1 | \phi_{i'_2} \wedge \ldots \wedge \phi_{i'_{n_2}} \hookleftarrow \Psi_2 \rangle = 0 \qquad \forall i_2, \ldots, i_{n_1}, i'_2, \ldots, i'_{n_2}.$$

Since, the $(n_1 - 1)$-particle functions, $\phi_{i_2} \wedge \ldots \wedge \phi_{i_{n_1}}$, span all of $\wedge^{(n_1-1)}\mathcal{H}$, and the $(n_2 - 1)$-particle functions, $\phi_{i'_2} \wedge \ldots \wedge \phi_{i'_{n_2}}$, span all of $\wedge^{(n_2-1)}\mathcal{H}$, the latter equation is equivalent to orthogonality between any pair of 1-internal functions, that is to say:

$$\mathcal{I}^1[\Psi_1] \perp \mathcal{I}^1[\Psi_2]$$

p-internal space of a wave function

Definition:

$$\mathcal{I}^p[\Psi] = \{\omega \in \wedge^p \mathcal{H}, \exists \Phi \in \wedge^{n-p}\mathcal{H}, \Phi \hookleftarrow \Psi = \omega\}$$

Example:

$$\Psi = \psi_1 \wedge \psi_2 \wedge \psi_3 \wedge \psi_4 + \psi_1 \wedge \psi_2 \wedge \psi_5 \wedge \psi_6$$

$$\downarrow$$

$$dim \mathcal{I}^1[\Psi] = 6 \quad \Rightarrow \quad dim \wedge^2 \mathcal{I}^1[\Psi] = 15$$

$$BUT \left\{ \begin{array}{lll} \psi_3 \wedge \psi_5, \psi_3 \wedge \psi_6, \psi_4 \wedge \psi_5, \psi_4 \wedge \psi_6 & \Rightarrow & 0 \\ \psi_3 \wedge \psi_4, \psi_5 \wedge \psi_6 & \Rightarrow & \text{linear} \quad \text{dependencies} \end{array} \right\}$$

$$\downarrow$$

$$dim \mathcal{I}^2[\Psi] = 10$$

p-orthogonality

Definition:

Let Ψ_1 be the wave functions of an n_1 electron group and Ψ_2 that of an n_2 electron group. Ψ_1 and Ψ_2 are said p-orthogonal if and only if:

$$\mathcal{I}^p[\Psi_1] \perp \mathcal{I}^p[\Psi_2]$$

Proposition (graded orthogonality):

If two states represented by the wave functions Ψ_1 and Ψ_2 are p-orthogonal then they are *a fortiori* q-orthogonal for all q such that, $inf(n_1, n_2) \geq q \geq p$.

This justifies the term “strong orthogonality”

p-orthogonality: Examples

Let $(\phi_i)_i$ be orthonormal spinorbitals.

Example 1: For integers, $n \geq p > 0$, the pairs, $\Psi_1 := \phi_1 \wedge \cdots \wedge \phi_{n-p} \wedge \phi_{n-p+1} \cdots \wedge \phi_n$ and $\Psi_2 := \phi_1 \wedge \cdots \wedge \phi_{n-p} \wedge \phi_{n+1} \ldots \wedge \phi_{n+p}$, are $(n - p + 1)$-orthogonal but not $(n - p)$-orthogonal since for $\Phi_1 := \phi_{n-p+1} \wedge \ldots \wedge \phi_n$ and $\Phi_2 := \phi_{n+1} \wedge \ldots \wedge \phi_{n+p}$, $\langle \Phi_1 \hookleftarrow \Psi_1 | \Phi_2 \hookleftarrow \Psi_2 \rangle = \langle \phi_1 \wedge \ldots \wedge \phi_{n-p} | \phi_1 \wedge \ldots \wedge \phi_{n-p} \rangle = 1$ is non zero, although $(\Phi_i \hookleftarrow \Psi_i) \in \mathcal{I}^{n-p}[\Psi_i]$, for $i \in \{1, 2\}$, by definition.

Example 2:
The functions $\Psi_1 := \phi_1 \wedge \phi_2 \wedge \phi_3 + \phi_4 \wedge \phi_5 \wedge \phi_6$ and $\Psi_2 := \phi_1 \wedge \phi_7 + \phi_2 \wedge \phi_8$ are 2-orthogonal (it is impossible to obtain Ψ_2 by annihilating a spinorbital in Ψ_1) but not 1-orthogonal since both ϕ_1 and ϕ_2 belongs to their one-internal space.

The Electronic Mean Field Configuration Interaction method

It consists in constructing successive, approximate, n-electron wave functions of the form:

$$\Psi = \Psi_1 \wedge \cdots \wedge \Psi_r \ ,$$

where $\Psi_i \in \wedge^{n_i}\mathcal{H}$, with $\sum_i n_i = n$, by means of a configuration interaction calculation in a basis set of group functions $\{\Psi_1^i \wedge \Psi_2^0 \wedge \cdots \wedge \Psi_r^0\}_i$ i.e., the wave functions of the first group functions are optimized in the mean field of the ground states of the other groups.

- The process can be iterated by switching to another group until self-consistence is achieved.

- Or/then a coarser partition of the n electron can be selected.

The Hopf algebra structure of $\wedge\mathcal{H}$

Exterior coproduct:

$$\begin{aligned} \mathcal{Y}:\wedge\mathcal{H} &\longmapsto \wedge\mathcal{H}\otimes\wedge\mathcal{H}\\ \psi_1\wedge\cdots\wedge\psi_n &\longrightarrow \mathcal{Y}(\psi_1\wedge\cdots\wedge\psi_n)=\sum_{I\in\mathcal{P}_n}\rho_{I,\bar{I}}\psi_{i_1}\wedge\cdots\wedge\psi_{i_p}\otimes\psi_{\bar{i}_1}\wedge\cdots\wedge\psi_{\bar{i}_{n-p}}\\ \Psi &\longrightarrow \mathcal{Y}(\Psi)=\sum_{I\in\mathcal{P}_n}\Psi_I\otimes\Psi_{\bar{I}}. \end{aligned}$$

The idea behind the coproduct is to split an n-fermion single configuration function into a p and an $(n-p)$-fermion single configuration functions in all possible ways, where p ranges from 0 to n, the exterior product of the two parts so-obtained giving back the initial function, the sign of the reordering permutation being taken care of.

As an example, let us write down the formula for $\mathcal{Y}$ acting on a 3-fermion configuration,

$$\begin{aligned} \mathcal{Y}(\psi_a\wedge\psi_b\wedge\psi_c) &= \psi_a\wedge\psi_b\wedge\psi_c\otimes 1+\psi_a\wedge\psi_b\otimes\psi_c-\psi_a\wedge\psi_c\otimes\psi_b\\ &\quad +\psi_b\wedge\psi_c\otimes\psi_a+\psi_a\otimes\psi_b\wedge\psi_c-\psi_b\otimes\psi_a\wedge\psi_c\\ &\quad +\psi_c\otimes\psi_a\wedge\psi_b+1\otimes\psi_a\wedge\psi_b\wedge\psi_c. \end{aligned}$$

Hopf algebra fundamental relation

$$\mathcal{Y} \circ \mathcal{X} = (\mathcal{X} \otimes \mathcal{X}) \circ (Id \otimes T \otimes Id) \circ (\mathcal{Y} \otimes \mathcal{Y})$$

where T is the twisting map:

$$\begin{array}{c} \forall \Phi \in \wedge^p \mathcal{H} \quad , \quad \forall \Psi \in \wedge^q \mathcal{H} \\ T(\Psi \otimes \Phi) \;=\; (-1)^{pq} \Phi \otimes \Psi. \end{array}$$

The fundamental Hopf algebra relation expresses the fact that the same decomposition of the product of two single configurations into a tensor product of 2 subconfigurations is obtained by applying the coproduct to the exterior product of the two single configurations, or alternatively, by first splitting each single configuration separately ($\mathcal{Y} \otimes \mathcal{Y}$), then grouping the first tensorial components of each decomposition together and the second components together ($Id \otimes T \otimes Id$), and finally by taking the exterior product of the first components on the one hand and the exterior product of the second components on the other hand ($\mathcal{X} \otimes \mathcal{X}$).

Convolution

$$A * B := \mathcal{X} \circ (A \otimes B) \circ \mathcal{Y}.$$

Ex: the Coulomb repulsion between two electrons, $V_{ee} = \frac{1}{||\vec{r_1} - \vec{r_2}||}$, is a 2-electron operator acting on $\wedge^2\mathcal{H}$, the convolution with the identity induces an operator on $\wedge\mathcal{H}$: $V_{ee} * Id$

Iterated products and coproducts

- kth iterated product

$$\mathcal{X}^{[k]} := \mathcal{X} \circ (\mathcal{X}^{[k-1]} \otimes Id) \ ,$$

with $\mathcal{X}^0 = Id$.

- kth iterated coproduct

$$\mathcal{Y}^{[k]} := (Id \otimes \cdots \otimes Id \otimes \mathcal{Y}) \circ \mathcal{Y}^{[k-1]} \ ,$$

We specify further by $\mathcal{Y}^{[k]}_{i_0,\dots,i_k}$ the component of the iterated coproduct corresponding to the decomposition of an n-Fermion wave function into the tensor product of $(k+1)$ wave functions of $i_0, \dots, i_k$-particles respectively.

Generalised twist operator

$T^{(p,q)}$, defined on the tensor product of $p.q$, (p and $q > 1$), Fermionic Hilbert spaces, $\wedge^{n_i^j}\mathcal{H}$, with fixed number of particles, n_i^j, $i \in 1, \cdots, p$ and $j \in 1, \cdots, q$.

Let $\Phi := \phi_1^1 \otimes \cdots \otimes \phi_p^1 \otimes \cdots \otimes \phi_1^q \otimes \cdots \otimes \phi_p^q$ be an element of $\wedge^{n_1^1}\mathcal{H} \otimes \cdots \otimes \wedge^{n_p^1}\mathcal{H} \otimes \cdots \otimes \wedge^{n_1^q}\mathcal{H} \otimes \cdots \otimes \wedge^{n_p^q}\mathcal{H}$,

$$T^{(p,q)}[\Phi] = \rho_{n_1^1,\dots,n_p^1,\dots,n_1^q,\dots,n_p^q}\ \phi_1^1 \otimes \cdots \otimes \phi_1^q \otimes \cdots \otimes \phi_p^1 \otimes \cdots \otimes \phi_p^q$$

where $\rho_{n_1^1,\dots,n_p^1,\dots,n_1^q,\dots,n_p^q}$ is the sign of the permutation which would reorder the tensorial components ϕ_i^j in their initial order if we had exterior products in place of tensor products. More explicitely,

$$\rho_{n_1^1,\dots,n_p^1,\dots,n_1^q,\dots,n_p^q} = (-1)^{\sum_{i=1}^{p-1}\sum_{j=2}^{q}\sum_{k=i+1}^{p}\sum_{l=1}^{j-1} n_i^j . n_k^l} .$$

In particular, $Id \otimes T \otimes Id = T^{(2,2)}$.

Generalised Hopf formula

The generalization of the Hopf algebra fundamental relation to the case of iterated product, $\mathcal{X}^{[p-1]}$, $(p > 1)$, and coproduct , $\mathcal{Y}^{[q-1]}$, $(q > 1)$, is,

$$\mathcal{Y}^{[q-1]} \circ \mathcal{X}^{[p-1]} = \underbrace{(\mathcal{X}^{[p-1]} \otimes \cdots \otimes \mathcal{X}^{[p-1]})}_{q factors} \circ T^{(q,p)} \circ \underbrace{(\mathcal{Y}^{[q-1]} \otimes \cdots \otimes \mathcal{Y}^{[q-1]})}_{p factors},$$

or for a particular coproduct component,

$$\mathcal{Y}^{[q-1]}_{n_1,\ldots,n_q} \circ \mathcal{X}^{[p-1]} = \sum_{n_i^j, \sum_{j=1}^{p} n_i^j = n_i} \underbrace{(\mathcal{X}^{[p-1]} \otimes \cdots \otimes \mathcal{X}^{[p-1]})}_{q factors} \circ T^{(q,p)} \circ \underbrace{(\mathcal{Y}^{[q-1]}_{n_1^1,\ldots,n_q^1} \otimes \cdots \otimes \mathcal{Y}^{[q-1]}_{n_1^p,\ldots,n_q^p})}_{p factors} .$$

Laplace formula

$$\langle \mathcal{X}(\Theta \otimes \Phi) | \Psi \rangle \equiv \langle \Theta \wedge \Phi | \Psi \rangle = \langle \Theta \otimes \Phi | \mathcal{Y}(\Psi) \rangle$$

Calculation of matrix elements between group functions

$$\langle \Phi_1 \wedge \Gamma_2 \wedge \cdots \wedge \Gamma_q | (h_2 * Id)[\Psi_1 \wedge \Gamma_2 \wedge \cdots \wedge \Gamma_q] \rangle$$

We set, $\Delta_{q-1} := \Phi_1 \wedge \Gamma_2 \wedge \cdots \wedge \Gamma_{q-1}$, $\Psi := \Psi_1 \wedge \cdots \wedge \Gamma_q$, and re-write the matrix element as:

$$\langle \Delta_{q-1} \wedge \Gamma_q | (h_2 * Id)[\Psi] \rangle =$$
$$\Sigma'_{n_k^l} \langle \Delta_{q-1} \otimes \Gamma_q | (\mathcal{X} \otimes \mathcal{X}) \circ T^{(2,2)} \circ (\mathcal{Y}_{n_1^1, n_2^1} \otimes \mathcal{Y}_{n_1^2, n_2^2}) \circ (h_2 \otimes Id) \circ \mathcal{Y}_{2,n-2}[\Psi] \rangle \, .$$

The constraints on the summation give rise to at most three terms:

- A term where the n_q-electron integral is an "h_2"-type integral and the $n - n_q$ electron integral is an overlap integral, when $n_1^1 = 0; n_1^2 = n - n_q; n_2^1 = 2; n_2^2 = n_q - 2$, provided that $n_q \geq 2$.
- A term where the n_q-electron integral is an overlap integral and the $n - n_q$ electron integral is a "h_2"-type integral, when $n_1^1 = 2; n_1^2 = n - n_q - 2; n_2^1 = 0; n_2^2 = n_q$, provided that $n - n_q \geq 2$.
- A term where the h_2 integral is splitted accross the n_q-electron and the $n - n_q$-electron integrals, when $n_1^1 = 1; n_1^2 = n - n_q - 1; n_2^1 = 1; n_2^2 = n_q - 1$.

Calculation of matrix elements between q-orthogonal group functions

$$\langle \Phi_1 \wedge \Phi_2 | \Psi_1 \wedge \Psi_2 \rangle = \langle \mathcal{X}\left[\Phi_1 \otimes \Phi_2\right] | \mathcal{X}\left[\Psi_1 \otimes \Psi_2\right] \rangle \quad (by\ definition)$$

$$= \langle \Phi_1 \otimes \Phi_2 | \mathcal{Y} \circ \mathcal{X}\left[\Psi_1 \otimes \Psi_2\right] \rangle \quad (by\ Laplace\ formula)$$

$$= \langle \Phi_1 \otimes \Phi_2 | (\mathcal{X} \otimes \mathcal{X}) \circ (Id \otimes T \otimes Id) \circ (\mathcal{Y} \otimes \mathcal{Y}) \left[\Psi_1 \otimes \Psi_2\right] \rangle$$

$$= \qquad (by\ Hopf\ algebra\ fundamental\ formula)$$

$$\sum_{\substack{I^1, I^2 \\ |I^1|+|I^2|=n_1 \\ |I^1| \in \{n_1-q+1,\dots,n_1\}}} (-1)^{|I^2|\cdot(n_1-|I^1|)} \langle \Phi_1 | (\Psi_1)_{I^1} \wedge (\Psi_2)_{I^2} \rangle \langle \Phi_2 | (\Psi_1)_{\bar{I}^1} \wedge (\Psi_2)_{\bar{I}^2} \rangle$$

Φ_1 q-orthogonal to $\Psi_2 \rightsquigarrow \sum_{i=n_1-q+1}^{n_1} \binom{n_1}{i}\binom{n-n_1}{n_1-i}$terms instead of $\binom{n}{n_1} = \sum_{i=0}^{n_1} \binom{n_1}{i}\binom{n-n_1}{n_1-i}$.

Convergence of the EMFCI method

Ground state energies in Hartree for LiH
(6-$31G^*$, full core calculations at 3.03642 au)

Step	0	1	2
geminal 1	-7.981090	-8.002268	
geminal 2	-8.001937		-8.003028

- HF energy: -7.98077 au.
- CCSD(T) energy: -8.00326.
- the antisymmetrized product of strongly orthogonal geminals (APSG) ansatz recovers only 33.5% of the CCSD(T) energy at the scf geometry (i.e. 3.03642 au) for the 6-311G** (5d orbitals) basis (Rosta and Surján, Int. J. Quant. Chem., **80**, p.96, 2000).

Accuracy of the NOG-SCF method

Lowest singlet energy levels of Beryllium in Hartree (6-31G*, 6d calculations)

state symmetry	Full CI (frozen core, 105 CSFs)	NOG-SCF (239 Coef.)	Full CI (4200 CSFs)
^{1}S	-14.613435	-14.616073	-14.616634
^{1}P	-14.388909	-14.390291	-14.393112
^{1}D	-14.311959	-14.312844	-14.316351
^{1}S	-14.222495	-14.223317	-14.226960
^{1}P	-14.144298	-14.145614	-14.148581
^{1}S	-14.106706	-14.108337	-14.109614
^{1}P	-14.038519	-14.039284	-14.043223
^{1}D	-13.931205	-13.932110	-13.935630
^{1}P	-13.895624	-13.896746	-13.900150
^{1}S	-13.800902	-13.802002	-13.805443

Coef.: Coefficients, CSFs: Configuration state functions.

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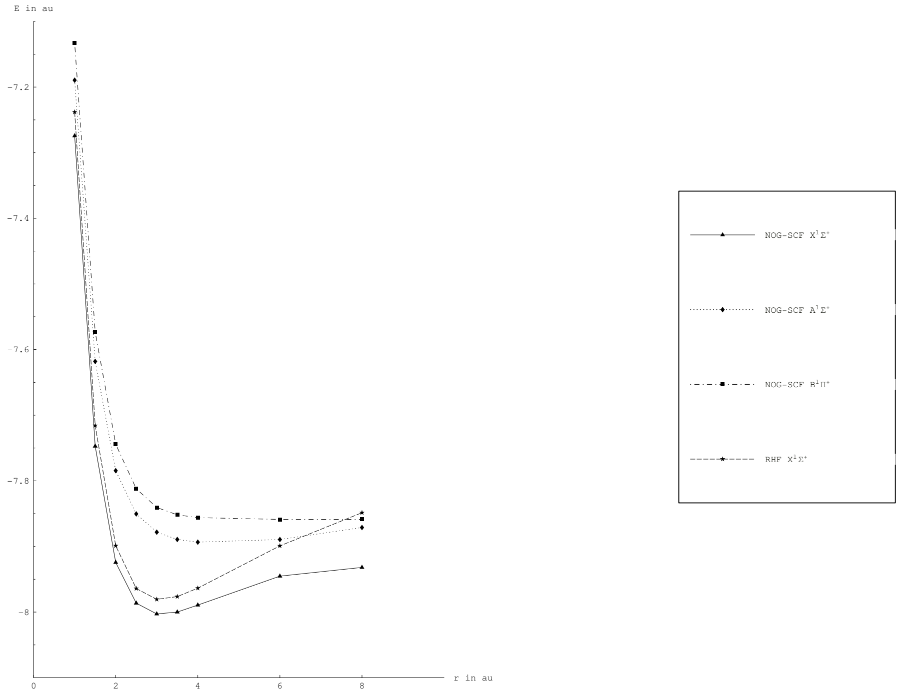
The Electronic MFCI method dissociates properly



Geminal-SCF and *p*-orthogonality

Ground state energies in Hartree at "experimental"[4] geometry
(STO-3G calculations)

System	Be	LiH	Li_2	BeH_2	BH
E^0_{FullCI}	-14.403655	-7.88239	-14.667340	-15.59486	-24.809945
$E^0_{geminal-SCF}$[1]	-14.403655	-7.88237	-14.667114	-15.59465	-24.809938
with 2-orthogonality [2]	-14.403654	-7.88237	-14.667084	-15.59435	-24.809920
with 1-orthogonality [3]	-14.403329	-7.88216	-14.666525	-15.57053	-24.778657
E^0_{RHF}	-14.351880	-7.86200	-14.638725	-15.55941	-24.752780

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[a] Upper bound after a large number of iterations; second derivatives are not calculated, the fact that the algorithm reaches a minimum cannot be ascertained. ; Truncation threshold for quasi-linear dependency of geminal products: 10^{-5} (Be, LiH) or 10^{-6} (Li_2, BeH_2, BH). Canonical HF initial guess.

[b] Two-orthogonality between each pair of ground state geminals.

[c] In fact, best step 0 energy, which can be considered in general as the G-SCF calculation with strong orthogonality constraint (1-orthogonality) within the present algorithm. The best strongly orthogonal G-SCF ground state would require to optimize the partitioning of the orbital Hilbert space between the different groups.

[d] From NIST website.

p-orthogonality: Conclusions - 1

- Graded measure of indistinguishability in the sense that two sets of identical particles that are q-orthogonal can be seen as “more indistinguishable” than two sets that are p-orthogonal if $q > p$, because a larger subset of particles can possibly share (i.e. occupy) a substate, common (i.e. internal) to the quantum states of both sets.

- p-orthogonality can be used to remove some arbitrariness in the choice of a representation for a quantum system in the same manner as localization criteria do: By setting, $g_i = \psi_i \wedge \bar{\psi}_i$ for all i, an HF function can be expressed as:

$$\Psi = g_1 \wedge g_2 \wedge \cdots \wedge g_n. \tag{1}$$

or with $g = (n!)^{-\frac{1}{n}}(\psi_1 \wedge \bar{\psi}_1 + \cdots + \psi_n \wedge \bar{\psi}_n)$, as:

$$\Psi = \underbrace{g \wedge g \wedge \cdots \wedge g}_{n factors}, \tag{2}$$

Imposing 2-orthogonality between the two-fermion functions appearing in Eqs.(2) and (1) can discriminate between these two equivalent writings.

p-orthogonality: Conclusions - 2

- The graded structure of p-orthogonality constraints naturally leads one to consider a corresponding hierarchy of approximations for methods based on general antisymmetric product functions.

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